Ultrasonics Sonochemistry 29 (2016) 388–393

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Sonochemical synthesis of Cu_2O nanocubes for enhanced chemiluminescence applications

Kulandaivelu Kaviyarasan [a], Sambandam Anandan [a,b,*], Ramalinga Viswanathan Mangalaraja [b], Thirugnanasambandam Sivasankar [c], Muthupandian Ashokkumar [d]

[a] Nanomaterials & Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Trichy 620 015, India
[b] Advanced Ceramics and Nanotechnology Laboratory, Department of Materials Engineering, Faculty of Engineering, University of Concepcion, Concepcion 407-0409, Chile
[c] Department of Chemical Engineering, National Institute of Technology, Trichy 620 015, India
[d] School of Chemistry, University of Melbourne, Parkville, Vic 3010, Australia

ARTICLE INFO

Article history:
Received 28 September 2015
Received in revised form 24 October 2015
Accepted 26 October 2015
Available online 26 October 2015

Keywords:
Cu_2O
Nanocubes
Sonochemical synthesis
Luminol
Chemiluminescence

ABSTRACT

A facile one-step sonochemical synthesis of Cu_2O nanocubes has been developed by ultrasound irradiation of copper sulfate in the presence of polyvinylpyrrolidone and ascorbic acid at pH 11. During sonication, the reaction between acoustic cavitation-generated radicals and $CuSO_4$ produced $Cu(OH)_2$ intermediate which then reacted with ascorbic acid to generate Cu_2O nanocubes. The products were characterized by FT-IR, XRD, HRTEM, AFM and particle size analyzer. The prepared Cu_2O nanocubes were found to be very effective for enhancing chemiluminescence in the presence of luminol–H_2O_2 system.

1. Introduction

The generation of copper(I) oxide (Cu_2O) with different size and morphology is still a challenging process. These materials are widely used in various applications such as solar energy conversion and catalysis [1–7]. Copper(I) oxide is an excellent p-type semiconductor material, has excellent optical absorption and luminescence properties [8]. Upon altering the size and morphology, the optical, chemical and physical properties of semiconductor materials could be improved [8–10]. Hence, many studies are devoted to synthesize materials with different morphologies (e.g., cubes, octahedral, rhombohedra, nanocages, hollow structures, porous structures, nanowires, etc.) for various applications in science and engineering [11–20].

In light of fast and growing applications of Cu_2O nanoparticles, the design of a facile and environmental friendly strategy is highly desirable. Many studies have reported on the preparation of Cu_2O with various morphologies using several methods [21–24]. For example, Kim et al. [25] reported synthesis of Cu_2O spheres through polyol approach employing poly(vinylpyrrolidone) (PVP) as a capping and stabilizing agent and use of chloride ion to promote the formation of a cubic morphology. Whereas Murphy and Gou [26] reported the synthesis of Cu_2O nanocubes in the presence of hydroxide ion by employing ascorbic acid as a stabilizing and reducing reagent. Xu et al. [27] synthesized Cu_2O nanospheres by combining biological reducing and capping agents (ascorbic acid and β-cyclodextrin, respectively) with ultrasound irradiation. Ultrasound irradiation produces a variety of physical and chemical effects in addition to providing unique environment for chemical reactions due to acoustic cavitation [28]. The aim of our investigation was to synthesis Cu_2O nanocubes via a sonochemical approach starting from copper sulfate pentahydrate employing polyvinylpyrrolidone (PVP) and ascorbic acid as stabilizing and reducing reagents, respectively without any promoting agents. In addition, we observed that the prepared Cu_2O nanocubes are found to be efficient for enhancing chemiluminescence of luminol–H_2O_2 system.

2. Experimental details

All chemicals were of highest purity available and used as received without further purification. Copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), luminol (3-aminophthalhydrazide), ascorbic acid and poly(vinylpyrrolidone) (PVP; MW 40000) were purchased

* Corresponding author at: Nanomaterials & Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Trichy 620 015, India.
E-mail address: sanand@nitt.edu (S. Anandan).

http://dx.doi.org/10.1016/j.ultsonch.2015.10.018
1350-4177/

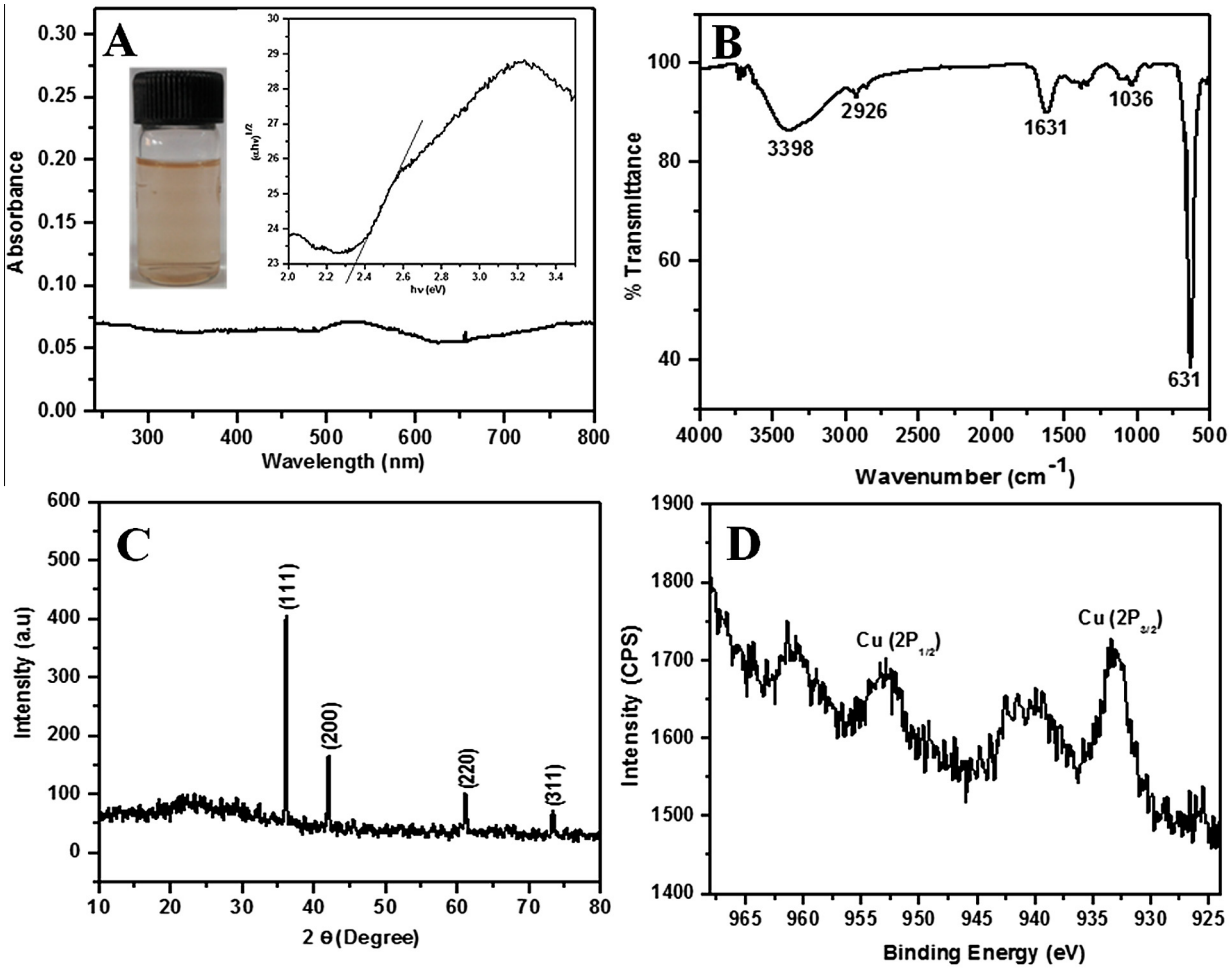

Fig. 1. Absorbance (A) FT-IR (B) XRD (C) XPS (D) spectrum of Cu_2O nanocubes. Insets in (A) show photographic image of prepared Cu_2Onanocubes and Tauc plot.

from Sigma–Aldrich. Unless otherwise specified, all the reagents used were of analytical grade and the solutions were prepared using millipore DDI water (18.2 MΩ).

2.1. Ultrasound assisted synthesis of Cu_2O nanocubes

Cu_2O nanocubes were synthesized via sonochemical reduction method. About 50 mL of copper sulfate pentahydrate (0.01 M) ($CuSO_4{\cdot}5H_2O$) was taken in a sonication vessel and nitrogen gas was purged for 30 min to remove dissolved oxygen. Subsequently, 52.8 mg ascorbic acid (0.01 M) dissolved in 15 ml of ethylene glycol was added slowly to the $CuSO_4{\cdot}5H_2O$ solution under vigorous stirring at room temperature for about 20 min. Ascorbic acid acted both as an antioxidant and reducing agent, i.e., it was employed as a protective agent to prevent the oxidation of Cu_2O to CuO [29]. Then 0.036 g PVP (stabilizing agent) was directly added to the above mixture with continuous stirring and then 20 mL NaOH (1 M) was added drop wise to maintain the pH around ~11. At this pH, the color of the mixture changed to green. The mixture was irradiated for 15 min with an ultrasonic horn (Sonics Ti-horn, 20 kHz, 100 W/cm^2). The green solution changed first to yellow and eventually to a deep orange color indicating the formation of Cu_2O nanocubes.

2.2. Characterization techniques

The attenuated total reflection (ATR) spectra of the prepared nanocubes were measured at room temperature by a Thermo Nicolet iS5 FTIR spectrophotometer ranging from 550 to 4000 cm^{-1}. The X-ray diffraction (XRD) patterns were recorded using Rigaku Ultima III diffractometer (Japan) with Cu-Kα radiation in the 2θ range from 10° to 80° by depositing the sample on a glass plate by spin coating. High resolution transmission electron microscopic (HR-TEM) images were recorded using JEOL JEM-2010 model. Energy dispersive X-ray (EDX) analysis was used to determine the elements present in the mixture. Atomic force microscopic (AFM) analysis (non-contact mode) was performed on a XE-100 scanning probe microscope, Park systems, South Korea. X-ray photoelectron spectroscopy (XPS) measurements were carried out using Physical Electronics PHI 5600 XPS instrument with monochromatic Al-Kα as (1486.6 eV) excitation source. Ultraviolet–visible absorption and chemiluminescence spectra were recorded on a Specord S 600 diode-array spectrophotometer and PL, Shimadzu, RF5301PC. Particle size and size distribution of Cu_2O nanocubes were analyzed using particle size analyzer (Malvern instrument, UK).

3. Results and discussion

Cu_2O nanocubes were synthesized in an ethylene glycol solution containing copper sulfate pentahydrate, PVP and ascorbic acid after ultrasonic irradiation for 15 min with 20 kHz Sonics horn type sonifier (100 W/cm^2) with a tip diameter of 13 and 25 mm (not provided in the manuscript) at room temperature (25 °C) by water circulation. While sonication for 15 min using 13 mm probe nanocubes are obtained whereas using 25 mm probe drastic particle